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TECHNICAL REPORT ECOM-01291-7

REVERSIBLE OXYGEN ELECTRODES

7TH QUARTERLY REPORT

By

J. O'M. Bockris
M. Genshaw
E. A. Beer
D. Sepa
Y. C. Chiu

April, 1967

ECOM

UNITED STATES ARMY ELECTRONICS COMMAND · FORT MONMOUTH, N.J.

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REVERSIBLE OXYGEN ELECTRODES

Report No. 7

Contract No. DA 28-043-AMC 01291 (E)

Task No. 1 CO 14501 A34A-00

SEVENTH QUARTERLY REPORT

For the Period

15 October 1966 - 14 January 1967

U. S. ARMY ELECTRONICS COMMAND

Fort Monmouth, New Jersey

Object: To conduct research on electrocatlysis, to determine the

mechanisms of oxygen reduction and to find the major factors

affecting the catalytic activity of the reaction so that a

reversible oxygen electrode may be developed.

Prepared by D. Sepa, Y. C. Chiu, E. A. Beer and M. Genshaw

Under the Direction of Professor J. O'M. Bockris, Principal Investigator

The Electrochemistry Laboratory
The University of Pennsylvania
Philadelphia, Pa. 19104

DISTRIBUTION STATEMENT

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PURPOSE

One of the pressing aims at pre. nt ... the development of technologically successful energy conver ion in electrochemical fuel cell systems is the finding of electrode materials on which, under given experimental conditions, the process of cathodic dissolution of oxygen can function sufficiently rapidly. The eventual objective of the study on oxygen electrodes is a "reversible oxygen electrode," i.e. one which works at a sufficient rate and a negligible overpotential.

The experimental program has been designed to determine the mechanism of oxygen reduction at various experimental conditions, and to find the major factors affecting the catalytic activity of the reaction. For this purpose, the O_2 reaction is studied on a number of metal electrodes and on various compounds stable in acid solutions and at high electrode potentials.

ABSTRACT

Small crystals of lithium, potassium and cesium tungsten bronzes were prepared. Also nonstoichiometric γ-tungsten trioxide was prepared. To study the catalytic activity of these bronzes a method of sintering them into gold was devised.

The homogeneous oxidation of iodide by oxygen was studied. The rate constant at 25° is 4×10^{-5} sec^{-1}. The reaction is first order in oxygen and zero order in iodide and hydrogen ions. The activation energy is 16.9 kcal/mole.

A very sensitive method of determining ion adsorption utilizing multiple reflection ellipsometry is suggested.

PUBLICATIONS, LECT" \ES, REPORTS AND CONFERENCES

A. Publications

A. Damjanovic, M. A. Genshaw and J. O'M. Bockris, "Distinction Between Intermediates Produced in Main and Side Electrodic Reactions", J. Chem. Phys., 45, 4057 (1966).

B. Reports

Quarterly Reports Nos. 1 through 6 on "Reversible Oxygen Electrodes," Contract No. DA 28-043 AMC-01291(E.).

C. Conferences

5 January 1967
The Electrochemistry Laboratory
University of Pennsylvania
Philadelphia, Pa. 19104

Present at the conference were Mr. J. A. Christopulos of the

U.S. Army Electronics Command and Dr. A. Damjanovic, Dr. M. Genshaw,

Dr. E. Beer, Mr. D. Sepa, Dr. Y. C. Chiu of the Electrochemistry Laboratory.

The experimental results of the last quarter and present plans of

the project were discussed.

I. CATALYSTS FOR OXYGEN ELECTRODE REACTION

1. Introduction

In attempts to solve why tungsten bronzes are catalysts for the oxygen reduction reaction, tungsten bronzes with other alkali metals, besides sodium, as well as bronzes of some other transition metals have to be investigated. However, all of these substances are available in the form of small crystals or powders, so a new type of electrode should be designed, which would enable examination of these materials as electro-catalysts for the oxygen reduction reaction.

1.1 Preparation of substances

Crystals of lithium, potassium and cesium tungsten bronzes were prepared by electrolysis of molten mixture of WO_3 and respective alkali tungstate, in a platinum crucible, at temperatures between 700 - 800°C, using a gold wire as cathode, on which these compounds were grown, at estimated current density of about 10^{-2} A cm^{-2}. The anode was a cylinder of gold sheet. Bronzes which resulted from these syntheses were in the form of very loose aggregates of small crystals, which separated completely through successive washing in hot solutions of 1 M NaOH and 1 M $HClO_4$.

Nonstoichiometric γ-tungsten trioxide was prepared also, using the thermal method of synthesis and solid state reaction between tungsten and tungsten trioxide. γ-WO_3 with a range of composition $WO_{2.65}$ - $WO_{2.76}$ has low resistivity (0.336 - 0.114 ohm cm., respectively) and is insoluble in acids, as is WO_3. Powders of WO_3 and tungsten were mixed in a ratio that corresponded to composition $WO_{2.7}$. The homogenized mixture of powders was pressed into a pill and put in a nickel boat in the furnace. Purified

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argon atmosphere was held in the furnace, heated at 800°C, during 24 hours. After cooling in the stream of argon, violet $WO_{2.7}$ was the result of synthesis.

Strontium niobium bronze and barium tantalum bronze were synthetized and kindly sent us from the Coal Research Center, Pittsburgh, United States Department of Mines. Sodium molybdenum bronze and sodium vanadium bronze were prepared in the Institute for Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia.

1.2 Electrode for powder-like electrocatalysts

Since all materials available were either powders or in the form of small crystals, they could not be examined in the same way as sodium tungsten bronzes were.[1] Therefore, an electrode had to be designed which would enable investigation of electrochemical properties of such powder catalysts.

It is known that gold is a very poor catalyst for the oxygen reduction reaction, but is very stable in acid media, especially if not oxidized. Using these properties of gold it was decided to press or sinter homogenized mixture of gold powder and the catalyst which is available in powder form. Gold powder, taken in excess, would surround very intimately grains of the substance investigated, and made excellent contact with them. By subsequent polishing or controlled dissolution of gold on the surface of such an electrode, a definite area occupied by the powdery substance would be opened, and catalyst could come in contact with electrolyte. Ratio of areas substance-gold on the surface of such an electrode could be easily determined under microscope on a representative

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piece of surface, and the total area of substance calculated.

Using very wide possibilities of sintering technique, a porous electrode can also be prepared in a similar manner.

2. Experimental

A mixture of gold and sodium bronze powder, in volume ratio 2:1 was pressed in a mold of specially hard steel (Fig. 1). Pressing was performed without heating, at room temperature, due to softness of gold and non-oxidized surface of gold. Using pressures from $4.3 - 9.3$ t cm^{-2}, excellent samples, concerning mechanical properties, were obtained.

3. Results

Higher pressure of pressing gives a sample with lower porosity. Less porous electrodes are more favorable because active area of surface could be equated to the calculated ratio of active substance in geometric area of electrode. For example, sample which was pressed with 9.3 t cm^{-2}, after one hour immersion in water, gained 0.75% of its weight, which, calculated to empty volume due to open pores, makes 5% of total volume. Experiment with pure gold powder, which was pressed with 7.0 t cm^{-2}, gave only 3% of volume filled with water (better packing of gold grains), but comparing densities of pressed sample and pure gold discrepancy was about 25%, which proves existence of closed pores inaccessible to the solution. The observed porosity of samples would not affect real working area of the electrode, because rate of reaction in pores would be strongly diffusion limited and cannot affect observed rate of reaction.

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4. Proposal for future work

First sample electrode with sodium tungsten bronze of known activity is just under investigation of electrochemical behavior. Using the same type of electrode powders of Li_xWO_3, K_xWO_3, Cs_xWO_3, $WO_{2.7}$, Na_xMoO_3, $Na_xV_2O_5$, Sr_xNbO_3 and Ba_xTaO_3 will be examined.

II.   REDOX CATALYSIS

1.   Introduction

The aim of this project is to improve the activity of the oxygen cathode by adding an intermediate to the electrolyte and thus changing the mechanism of oxygen reduction.   The intermediate must be a redox system.

As discussed in a previous report[2] there are three basic requirements for this action.   The chosen redox couple must

    a. have a high redox potential

    b. undergo reduction at the electrode at a high rate

    c. react with oxygen readily.

Early experiments and literature data show that it is possible to find redox systems that satisfy the first and second requirements.   But all of these systems react with oxygen too slowly.   Therefore the third point is the most crucial one of all three and research work should be concentrated on it.

For this reason in the previous quarter the homogeneous oxidation of several redox couples was investigated.   In particular, results

4.

concerning the kinetics of the reaction

$$4Fe^{2+} + O_2 + 4H^+ \rightleftarrows 4Fe^{3+} + 2H_2O \qquad (1)$$
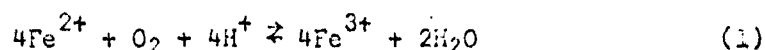
was presented.

Keeping the emphasis on the homogeneous oxidation, during this present reporting period an attempt was made to elucidate the kinetics and mechanism of the oxidation of the redox system I^-/I_2

2. Experimental

For the measurement of oxidation rates the gas-volumetric apparatus introduced earlier[3] was used. It was designed to make possible the observation of all reactions involving the consumption or evolution of oxygen (or another gas). Its limitations include the inability to measure reactions with two gaseous species; but these process are a priori of no interest to the project.

Also the rate of reaction must be within certain limits if the mentioned apparatus is to be applied uscessfully. Processes consuming or producing less than about 3.10^{-9} mol l^{-1} sec^{-1} oxygen do not yield sufficiently precise results; but these are too slow for catalytic purposes in any case. Reactions faster than about 10^{-6} mol l^{-1} sec^{-1} (in terms of O_2 consumption) are also hard to follow, but by adjusting the experimental conditions (mainly concentration and temperature) even these can be measured.

The oxidation of KI does not approach any of the limitations mentioned above, therefore no difficulties were encountered.

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3. Results

The equation for the oxidation of KI is

$$4I^- + O_2 + 4H^+ \rightleftarrows 2I_2 + 2H_2O \tag{2}$$
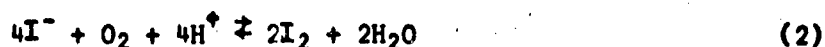
The rate constant of the reaction at 40°C is $k_2 = 4:10^{-5}$ sec^{-1}, as calculated for a first order reaction.

The reaction is first order in respect to the partial pressure of oxygen, as Fig. (2) shows. The order of reaction in respect to the hydrogen ion concentration is close to zero for pH 0.2 to 2.3 and first order for pH > 2.3 (Fig. 3).

In respect to iodide ions, the reaction is also near zero order.

Thus the overall order of the reaction appears to be 1 at hydrogen ion concentrations above 0.01.

From measurements of the rate constant at different temperatures (Fig. 4), we can calculate the activation energy of the reaction using Arrhenius' equation. For the homogeneous oxidation of potassium iodide it is $E_A = 16.9$ kcal/mole.

A set of experiments was made to determine possible catalytic activity of activated charcoal on this oxidation process. At 40°C in a 6 M KI solution (pH=0.3) the rate constant increased four times upon addition of 1 g/l activated charcoal.

The investigation of the system is not yet finished, more points are needed to ascertain the correctness of the above data. Particularly important are further measurements with possible catalysts.

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4. Discussion

The basic problem presented by the highly irreversible oxygen electrode is a kinetic one. In the oxidation process of several redox couples there is a very slow rate-determining step. As a result, oxygen practically does not oxidize its more negative neighbors in the table of standard oxidation potentials, although thermodynamic considerations lead us to expect this.

The mechanisms of these reactions do not necessarily consist of the same steps, but the fact that no oxdiation could be observed with systems having a redox potential higher than about 0.8 V (E_o = 1.23 V for OH^-/O_2) confirms the speculation that the same high-energy step is involved in all of these cases.

A very plausible suggestion concerning the rate-determining step is that of Latimer.[4] He points to a possible explanation by assuming that the first step of some oxidation reactions is the reduction of O_2 to H_2O_2, for which the standard redox potential is 0.68 V. This would make impossible any oxidation by oxygen beyond about 0.7 Volt and would explain the relative slowness of the ferrous-ferric reaction reported earlier.[3] It also agrees with the present data on the oxidation of KI. The I^-/I_2 system has a standard redox potential of 0.53 V. The difference between this and 0.68 V is greater than in the case of Fe^{2+}/Fe^{3+}; therefore, in the absence of complications in the mechanism, a faster reaction would be expected. Actually, under similar conditions the oxidation rate constant is indeed about 2.2 times greater than that for Fe^{2+}.

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The system I^-/I_2, beside its immediate use as a redox catalyst, offers the chance to learn more about the reaction mechanism of oxidation by oxygen. This is necessary for the basic understanding of the irreversibility of the oxygen electrode and for any improvement of it.

III. THE DETERMINATION OF CATION ADSORPTION IN THE
OXYGEN REDUCTION IN ALKALINE SOLUTION

1. Introduction

The reduction of oxygen on platinum in alkaline solutions occurs through H_2O_2 as an intermediate.[5] This can be represented as:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \qquad (1)$$

$$HO_2^- + H_2O + 2e^- \xrightarrow{k_2} 3OH^- \qquad (2)$$
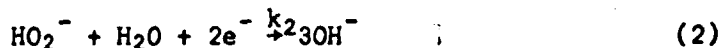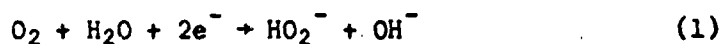
It was found that the addition of small quantities of the cations Ca^{++}, Sr^{++} and Ba^{++} changed the rate of the reactions.[1,6,7] The total reduction current was found decreased several times while the k_2 value increased an order of magnitude.[1] This effect was tentatively explained by the adsorption of the cations on the oxidized platinum surface.[6] The problem was further investigated by some Russian workers[8] using radiotracer method to determine the amount of Ca^{++} and Ba^{++} adsorbed on the platinum surface. The effect was explained by the formation of stable compounds between the cations and oxides of platinum. However, the experimental method they used involved some uncertainty in the determined amount. According to their procedures, the adhering solution containing radioactive materials was corrected for by weighing the solution and the electrode together and

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then substrating the dry weight of the electrode without counting the evaporation of the solution while weighing. Since the adhering solution is always a problem in the radiotracer method of studying adsorption and there is not any satisfactory method existed at the present for the study of ion adsorption, at relatively high concentrations, there is an urgent need to have a new method developed for this purpose. It is the aim of this work to develop a reliable method for determining ion adsorption and to explain the effect of the cations on the oxygen reduction through the result of the adsorption study. After many considerations and discussions with the experienced workers in this laboratory ellisometry was chosen to be a very promising method for this study.[19-11] Ellisometry has long been proven to be a highly accurate and non-destructive method for surface study. It has the advantage of making available a simultaneous study of the electrochemical reaction and the adsorption phenomenon. This method has been developed to study the oxygen-containing films on platinum electrodes[12] and the passivation of nickel[13] in this laboratory.

2. <u>Experimental</u>

According to other workers,[8] the maximum coverage of Ba^{++} on platinized platinum is about 15% of a monolayer. In order to see such a small amount of Ba^{++} adsorbed on the electrode surface, an extremely good sensitivity of the ellisometer is required. For this reason, a few modifications have been made to the ordinary ellisometry:

1. A laser is used as the light source to obtain an intense, monochromatic and parallel beam.

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2. Multiple reflection is employed to enhance the effect due to the small amount of adsorption.

With these modifications, it is expected that 1% of precision could be obtained in the determination of Ba^{++} adsorption provided that the ellisometer is sensitive to $\pm0.01°$. Since the sensitivity of the instrument is the major factor governing the success of the experiment, most of the initial effort has been devoted to increase the sensitivity of the ellisometer during this reporting period.

The laser was produced by Optics Technology Inc. (Model 170). The ellisometer used in the experiment is a Gaertner Model L119 (Gaertner Optical Instrumentation.) This instrument is designed primarily for the mercury light source with a wavelength of 5641 $\overset{o}{A}$.

Two pieces of platinum surfaces made by sputtering technique on glass substrate were used in the preliminary experiments reported here. The two surfaces were made parallel with a distance of 1 mm from each other. The region for the multiple reflection was about 1 cm wide across the surfaces. The experiments were done in air.

The polarizer, quarter-wave plate and analyzer were aligned to $\pm0.02°$ by first calibrating the analyzer with the reflected light from a quartz surface at the Brewster angle of incidence when the quarter wave plate was removed and then finding the extinction position of the light by turning the polarizer and later the quarter-wave plate when both arms of the instrument were in a straight-through position.

3. Results

It was found from these preliminary experiments that the required

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precision is obtainable by using multiple reflection provided that the
following conditions are fulfilled:

(1) The surfaces used in the reflection of light are clean and smooth.

(2) A small point source of light (with a maximum diameter of 1mm)
is impinged upon the surfaces.

(3) The light doesn't penetrate through the surfaces and cause
diffusing light spread around the main reflected beam.

(4) Since the sensitivity is proportional to the ratio of the
change of intensity of light to the change of the position of the quarter-
wave plate and analyzer, the reflected light should have the intensity
ratio of its maximum to minimum values, obtained by changing the position
of the quarter-wave plate and analyzer, to be greater than three orders
of magnitude.

Under the above conditions, reflected light from two parallel
platinum surfaces at 9 reflections was measured to the sensitivity of
$\pm 0.02^{\circ}$.

4. Plan for the Future

From the results obtained in the preliminary experiments, the
following plans were made for the next step of the measurement:

(1) Freshly prepared, smooth platinum surfaces made by vacuum
deposition technique will be used in the measurement.

(2) Since the quarter-wave plate and photo-multiplier were
designed for the mercury light, it may prove neccessary to change these
parts to the corresponding ones designed for laser beam.

(3) A cell suitable for both electrochemical and optical measurements will be designed and manufactured.

(4) Successive improvement to the equipment as well as to the experimental technique for obtaining better precision will be carried on upon each subsequent experimental result.

(5) Although the ellisometry technique described here is primarily designed for the determination of ion adsorption, there is no good reason to deny its general applicability to the adsorption of any other substances, since there is no special condition concerning the specific property of the system (such as charge, mass, physical state, concentration, etc.) has been imposed upon the technique itself. The success of ellisometry technique in the determination of ion adsorption will serve as a very good starting point in obtaining a general method for adsorption study even for a very small amount adsorbed.

IV. REFERENCES

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12. Report No. 8 (1963), U. S. Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey, Task No. 3A 99-09-001-02.

13. B. Rao, Ph.D. Thesis, Department of Chemistry, University of Pennsylvania, 1966.

V. PROJECT PERSONNEL

The following personnel performed the approximate number of man hours of work as follows:

John O'M. Bockris   Estimated 33 man hours

   Project Director with academic background in physical electrochemistry.

   B.S. in Physical Chemistry, Imperial College (London)

   Ph.D. in Physical Chemistry, Imperial College (London)

   D.Sc. University of London

Aleksender Damjanovic   Estimated 300 man hours

   Project Supervisor with academic background in physical chemistry and physical metallurgy.

   B.S. in Chemical Engineering, Belgrade University.

   Ph.D. Cavendish Laboratory, Cambridge University.

Marvin Genshaw   167 man hours

   B.S. Chemistry, Michigan College of Mining and Technology.

   Ph.D. in Chemistry, University of Pennsylvania.

Darko Sepa   500 man hours

   M.S. Ch.M.E., University of Belgrade.

Endre Beer   500 man hours

   M.S. Chemistry, Technical University, Hungary, 1956.

   Ph.D. Chemistry, Technical Hochschule, Darmstadt, Germany, 1963.

Ying-Chech Chiu   500 man hours

   B.Sc. in Chemical Engineering, Cheng Kung Univ., Taiwan.

   Ph.D. in Chemistry, Baylor University.

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Technicians

Charles Searles	75 man hours
Henry Hudson	50 man hours
Niel Nathanson	11 man hours
Ray Dolgert	13 man hours

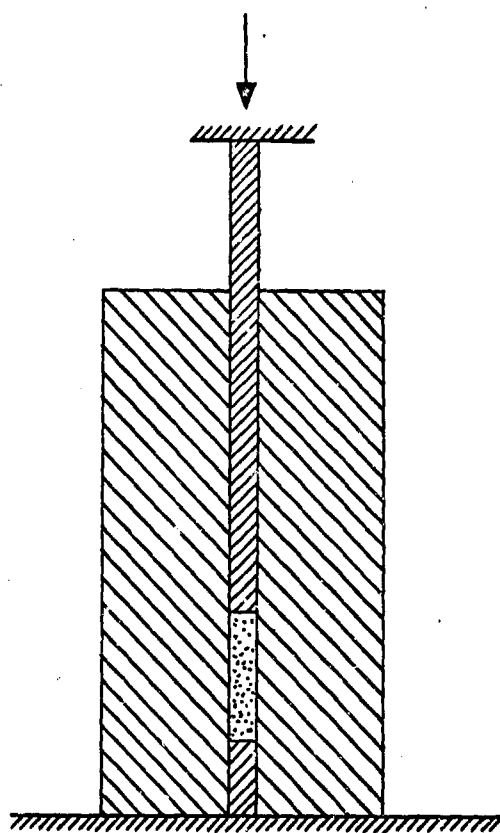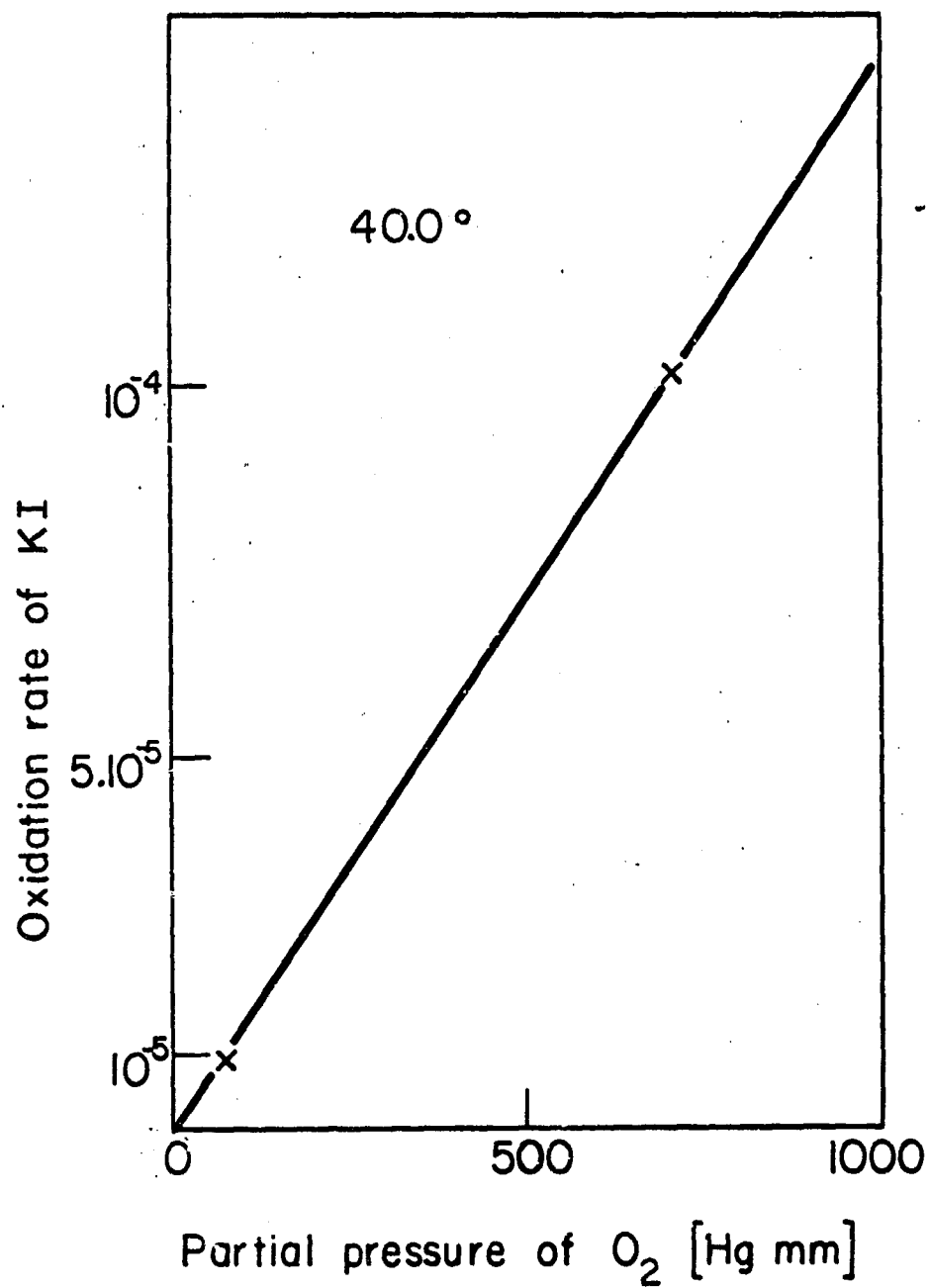FIG. I Mold for pressing mixture of gold and bronze powders.

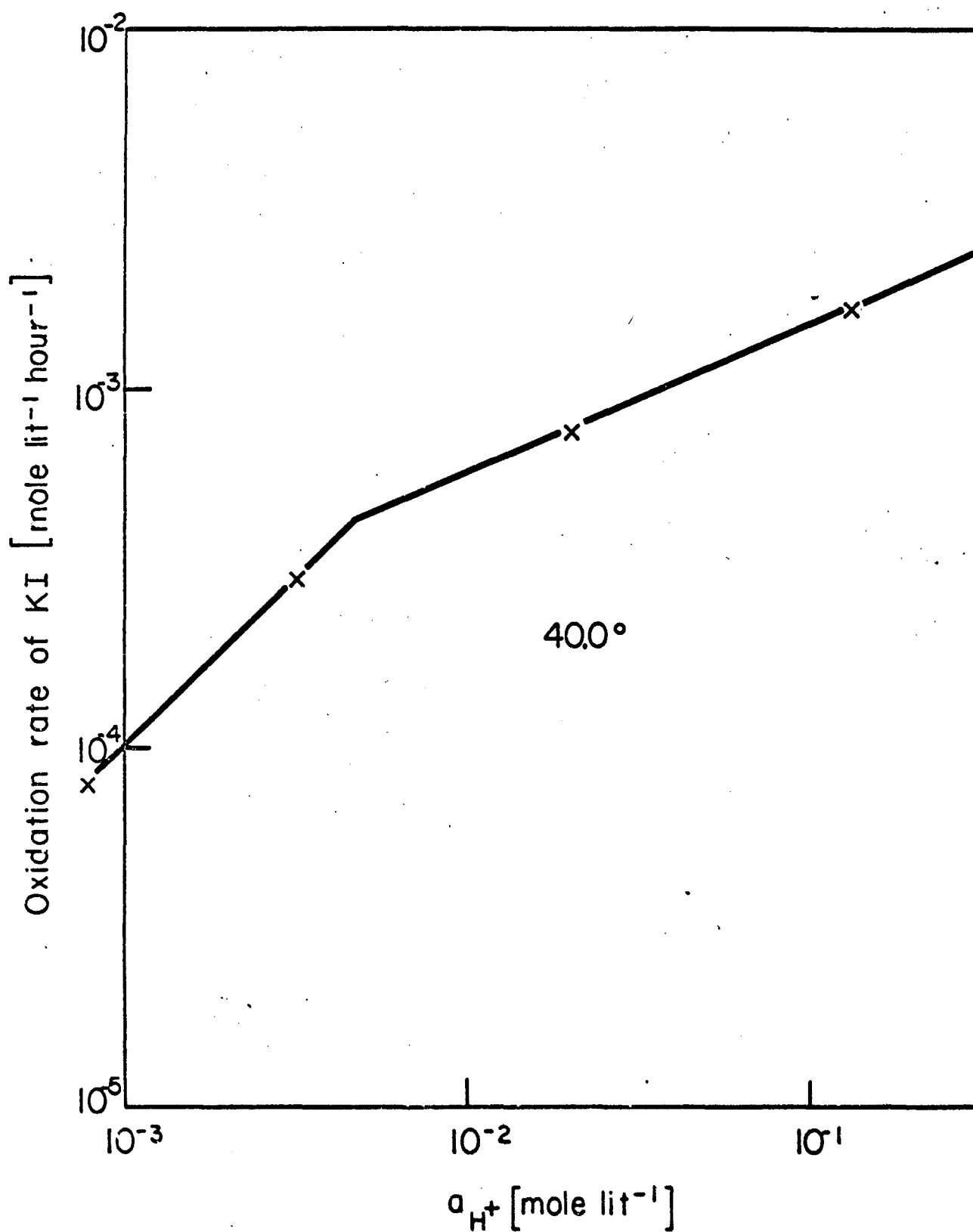FIG.2 Dependence of reaction on oxygen pressure

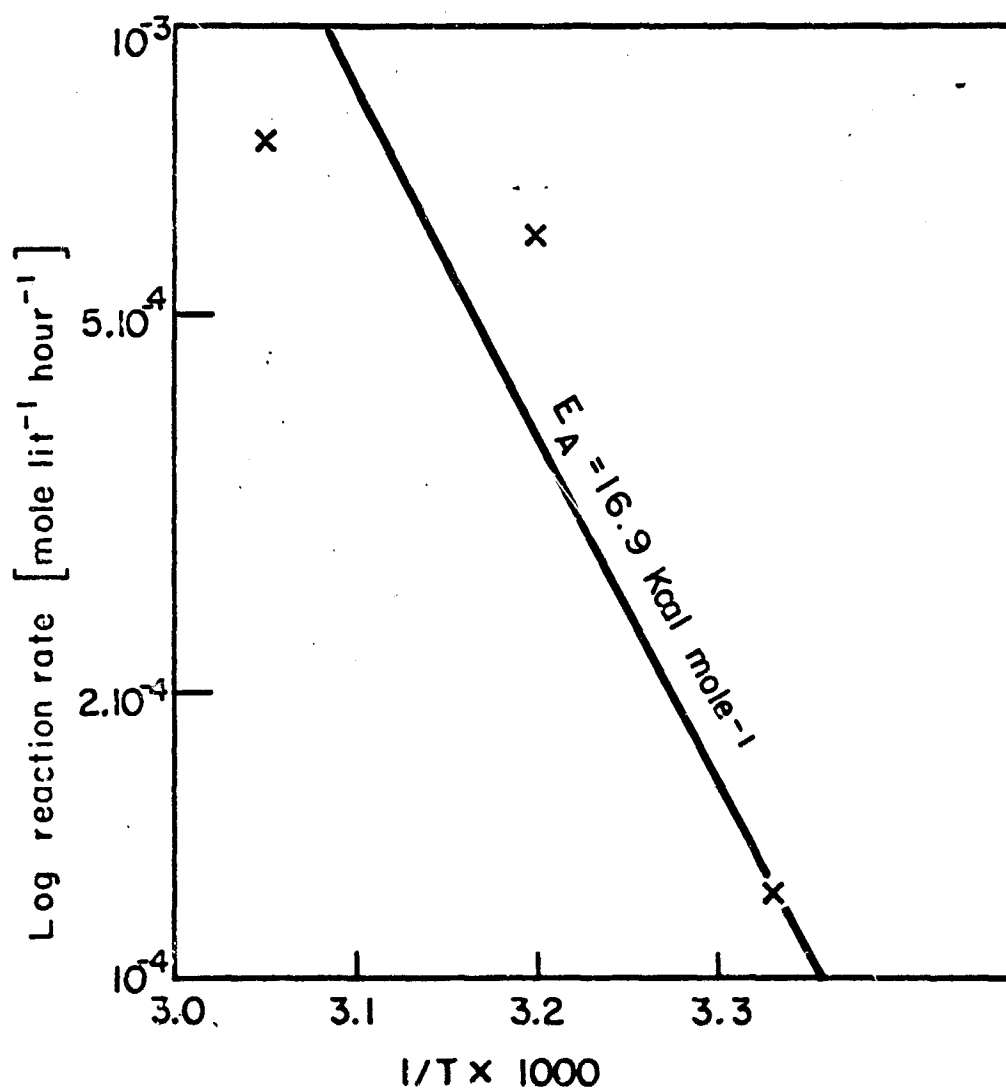FIG. 3 Dependence. of reaction rate on hydrogen ion activity.

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FIG.4 Plot for determining activation energy

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13. ABSTRACT

Small crystals of lithium, potassium and cesium tungsten bronzes were prepared. Also nonstoichiometric γ-tungsten trioxide was prepared. To study the catalytic activity of these bronzes a method of sintering them into gold was devised.

The homogeneous oxidation of iodide by oxygen was studied. The rate constant at 25° is 4×10^{-5} sec $^{-1}$. The reaction is first order in oxygen and zero order in iodide and hydrogen ions. The activation energy is 16.9 kcal/mole.

A very sensitive method of determining ion adsorption utilizing multiple reflection ellipsometry is suggested. (Authors)

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Oxygen Electrode						
Electrode Catalysts						
Oxide Materials (Perovskite Type)						
Tungsten Bronzes						
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